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# Configurational bias Monte Carlo: a new sampling scheme for flexible chains

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We propose a novel approach that allows efficient numerical simulation of systems consisting of flexible chain molecules. The method is especially suitable for the numerical simulation of dense chain systems and monolayers. A new type of Monte Carlo move is introduced that makes it possible to carry out large scale conformational changes of the chain molecule in a single trial move. Our scheme is based on the selfavoiding random walk algorithm of Rosenbluth and Rosenbluth. As an illustration, we compare the results of a calculation of mean-square end to end lengths for single chains on a two-dimensional square lattice with corresponding data gained from other simulations.

## 1. Introduction

A potential advantage of the Monte Carlo (MC) simulation method is its great flexibility. In molecular dynamics (MD) simulations, equilibrium averages are sampled by following the natural time evolution of a many-body system. In contrast, the MC technique allows for 'unphysical' moves in configuration space. Such moves may correspond to transformations that only take place over very long times in MD simulations. This added flexibility of the MC method is, for instance, exploited in the study of phase equilibria in the Gibbs ensemble [1]. For the special case of simulations of flexible chain molecules, for example alkanes or polymers, the MC method has the added advantage that simplified but very fast simulations on lattice systems are possible.

Nevertheless, the existing Monte Carlo methods of sampling chain-molecule configurations do have certain disadvantages that limit their use. For polymer simulations, the crucial problem is to achieve configurational equilibrium, i.e., a situation in which different conformations of the chain molecules appear with the correct statistical weight. How rapidly this equilibrium situation is attained depends on the nature of the trial moves employed during the simulation. Clearly, the standard translational and rotational moves of the entire molecule do not affect the molecular conformation. Hence, additional trial moves are needed to change the conformation. The simplest method to achieve this, at least in principle, is by rotation around single bonds [2]. However, such trial moves are not very efficient for all but the shortest chain molecules, because even a small rotational displacement around one bond may

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lead to a large displacement of distant parts of the same molecule. As a consequence, any attempt to generate a substantial conformational change through such trial moves is likely to result in an inter- or intramolecular overlap.

Over the past two decades, much effort has been devoted to the development of more efficient schemes to sample the different conformations of chain molecules. Most of these schemes are limited to chain molecules on a lattice. An extensive review is given by Kremer and Binder [3]. Unfortunately, many of these more sophisticated sampling methods break down for dense polymer systems, and those methods that would work at high densities, such as the bond breaking schemes of [4] and [5], are limited to polydisperse systems. Recently, Pakula *et al.* [6] proposed a Monte Carlo trial move for monodisperse systems that should work up to a reduced density of unity. The reduced density is defined as the ratio of the number of occupied lattice sites to the total number of lattice sites, e.g., a reduced density of unity corresponds to a system where no empty lattice sites exist. However, this scheme involves a rather complicated sampling procedure to move localized topological defects in chain molecules on a lattice.

For monolayer systems the choice of an efficient configurational move is even more problematical. This is so because many of the more successful schemes to sample bulk systems, in particular those involving 'reptation' moves [3, 7], are based on an approach where the molecular conformation can only change if the molecule as a whole is moving. Such algorithms are of no use for the study of monolayers, where one end of the molecule is fixed.

One possible remedy for the problems above is to employ trial moves that involve cooperative bond rotations. Such moves are designed to change the conformation of a chain molecule locally or even globally. A sampling scheme of this kind would be most efficient if the new trial conformation were generated by completely reassembling the chain molecule or part thereof. In analogy with the force-bias Monte Carlo scheme [8], it is preferable to bias the underlying Markov chain of the MC schemes towards generating more probable configurations with a higher frequency. This is important, because reassembling the chain molecule completely at random will, in the overwhelming majority of cases, result in energetically unfavourable configurations. It is therefore important to generate the trial conformation in a 'smart' way, i.e., in such a way that it avoids both itself and other chains in the system and takes other intramolecular potentials, like the *trans–gauche* torsional potential, into account. We suggest that the (self-) avoiding random walk (SAW) scheme of Rosenbluth and Rosenbluth [9] can be modified in such a way that it meets these requirements. To be more precise, we shall use the ratio of the 'Rosenbluth' weight factors of the new and old conformation to decide if a trial move should be accepted. Below, we discuss the approach on which this sampling scheme is based in some detail. In particular, we show that it satisfies the condition of *detailed balance*, and that it does indeed allow us to generate appreciable changes in molecular conformation in a single trial move.

## 2. Configurational-bias Monte Carlo

In the present section we explain the structure of the new sampling scheme. For the sake of clarity we follow the original Rosenbluth work [9] by considering a system of 'hard-core' polymers on a lattice. In fact, all results reported in the present communication were obtained for this particular model system. It should be stressed,

however, that neither the use of a lattice model nor the choice of the hard-core interaction is essential. This point was already discussed by one of us in a previous paper [10], where it was shown that the Rosenbluth self-avoiding random walk scheme can be easily extended to arbitrary molecular systems.

In the course of a Monte Carlo simulation, we allow for the 'conventional' translational and rotational moves of the entire polymer chain. The novel feature of the current Monte Carlo scheme is the way in which we attempt to change the conformation of the individual molecules. The initial steps of this new trial move consist of the random selection of a chain molecule ($i$, say) and a segment ($j$, say) in this molecule. We then discard all units in the chain molecule with indices larger than $j$ (or, with equal probability, smaller than $j$). Next, we attempt to regrow the same length of chain using the Rosenbluth (self-) avoiding random walk algorithm. This algorithm proceeds as follows.

1. Check if any of the lattice sites neighbouring the current end point of the growing chain are unoccupied. The chain growth can only continue if at least one neighbouring position is not occupied either by other molecules in the system or by any previous unit of the trial chain that we are growing.
2. From these available positions, one is chosen at random and the next segment of the trial conformation is added at this position. The new Rosenbluth weight for the trial conformation of length $m$ is calculated following the original scheme

$$W_m = (n'/n)W_{m-1}, \tag{1}$$

with $n$ the maximum number of choices (number of next-nearest neighbour sites except the one corresponding to the previous unit, which is dependent only on the type of lattice used in the simulation and the geometrical requirements for the test molecule), $n'$ the number of available sites for the walk, and $m$ the number of the new unit. $W_0$, the Rosenbluth weight at the start of the regrowth sequence, is equal to the Boltzmann factor of the point where the regrowth starts. In the example that we consider, $W_0 = 1$. In the case that no free neighbour sites are available, the corresponding weight for the trial attempt is zero and the attempt to grow a trial conformation has to be abandoned.
3. Otherwise we proceed with steps 1 and 2 until the desired length of the trial chain is reached.
4. Finally, we have to decide if we accept the outcome of the selfavoiding random walk as a new trial conformation. Below we discuss two criteria to decide whether or not a trial conformation is accepted. As we shall show, very good results are obtained with one of these criteria: namely, the one based on the ratio of the Rosenbluth weight of the trial conformation and the old conformations

$$P_{\text{acceptance}} = W_{\text{trial}}/W_{\text{old}}$$

(see (8) below). The above test is completely analogous to the corresponding test in the force-bias MC scheme [2, 8] (see below). Having accepted the SAW outcome as a trial move, we proceed to calculate the energy of the old and new configurations and use the standard Metropolis acceptance criterion [11] to decide if our system changes from the old into the trial configuration.

Actually, it is usually advantageous to extend the scheme described above and

include *all* contributions to the Boltzmann weight of the chain conformations already in the Rosenbluth weight factor. We can use the Boltzmann weights of the neighbouring positions during one step of the walk to bias the random choice of the next unit and therefore generate chains with a higher statistical weight more often. Instead of choosing one of the $n'$ available sites for the walk with equal probability as is the case in the original selfavoiding random walk scheme [9], we now select the next position $j$ with a probability

$$P_j = \frac{B_j}{\Sigma_{i=1}^{n} B_i}, \tag{2}$$

with $B_j$ the Boltzmann weight of the position that is actually chosen at random, and $\Sigma_{i=1}^{n} B_i$ the sum of the Boltzmann weights of all the $n$ neighbouring positions. In practice, the test described in (2) is carried out as follows. We divide the interval $\{0, 1\}$ into $n$ nonoverlapping segments of length $P_1, P_2, \ldots, P_n$ (as the $P_j$'s are normalized these segments cover the entire interval $\{0, 1\}$). We now draw a random number $r$ between 0 and 1. If $r$ is located in segment $j$, then we accept position $j$ as the next step in our trial conformation. Clearly, the probability that $r$ falls in segment $j$ is equal to $P_j$. If we use equation (2) to generate trial conformations, then we must change the expression for the Rosenbluth weight (equation (1)) to

$$W_m = \frac{\Sigma_{i=1}^{n} B_i}{n} W_{m-1}. \tag{3}$$

Here, $\Sigma_{i=1}^{n} B_i$ is the equivalent of $n'$ of equation (1). A biased (self-) avoiding random walk of a similar type has been successfully employed in previous simulations [12, 13].

The use of a selfavoiding random walk to generate a trial conformation is crucial because such a SAW is biased towards non-overlapping conformations. Such a procedure therefore obviates the need to sample large numbers of inaccessible conformations. It should be stressed that, because we use the Rosenbluth weight factor as a bias in the MC scheme, all chain conformations are generated with the correct statistical weight.

Following the normal procedure for smart Monte Carlo schemes to generate the underlying Markov chain [2], we can use a standard rejection technique to decide on the acceptance of the SAW outcome as a trial conformation. A trial move will be accepted if

$$\text{rand}(0; 1) \leqslant W_{\text{trial}}, \tag{4}$$

with rand(0; 1) a random number between 0 and 1, and $W_{\text{trial}}$ the Rosenbluth weight of the trial conformation. If the trial conformation is rejected, the 'new' chain conformation is simply equal to the old conformation, just as in the usual 'Metropolis' Monte Carlo scheme. It is easy to show that the acceptance criterion given by (4) satisfies the Monte Carlo conditions of *detailed balance* and *microscopic reversibility*. Consider two acceptable chain conformations, $m$ and $n$. We wish to compute both the transition probability $\alpha_{mn}$ that a trial move in the configurational bias scheme will transform $m$ into $n$ and the transition probability $\alpha_{nm}$ for the reverse move. From the discussion above it follows that $\alpha_{mn}$ and $\alpha_{nm}$ are given by

$$\begin{aligned} \alpha_{mn} &= P_n W_n \\ \alpha_{nm} &= P_m W_m, \end{aligned} \tag{5}$$

where $P_m$ is the (unweighted) probability that the Rosenbluth selfavoiding random walk algorithm will generate configuration $m$, while $W_m$ is the corresponding Rosenbluth weight. Attention should be drawn to the fact that here the index $m$ for the Rosenbluth weight stands for the corresponding weight of the conformation $m$ and not, as in equations (1) and (3), for the current length of the trial SAW. Let us denote the probability of finding the chain molecule in state $m$ or $n$ by $\rho_m$ and $\rho_n$. To check for *detailed balance* we now compute the ratio of the transition rates from $m$ to $n$ and backwards:

$$\frac{K_{mn}}{K_{nm}} = \frac{\rho_m P_n W_n}{\rho_n P_m W_m}. \tag{6}$$

The Rosenbluth scheme ensures that

$$\frac{P_m W_m}{P_n W_n} = \frac{\rho_m}{\rho_n}; \tag{7}$$

and hence it follows that *detailed balance* is fulfilled, i.e., $K_{mn} = K_{nm}$.

There is, however, a practical problem associated with the use of the rejection as in equation (4) to determine acceptance of trial SAWs, because at high densities and for long chain molecules most Rosenbluth weights for trial conformations will be quite small and hence acceptance of the trial conformation is very unlikely. The sampling efficiency can be improved appreciably by making the probability of acceptance of a trial conformation dependent on the ratio of the Rosenbluth weights for the new and the old conformations, analogous to the acceptance criterion of Metropolis Monte Carlo. The acceptance criterion from equation (4) changes now to

$$\text{rand}(0; 1) \leqslant W_{\text{trial}}/W_{\text{old}}. \tag{8}$$

The computation of the Rosenbluth weight of the old conformation, $W_{\text{old}}$, proceeds in close analogy to the generation of a trial conformation. However, instead of building up the conformation from one segment to the next, we simply compute the corresponding weight factors while tracing the 'actual' path of the chain molecule. It is easy to show that this slightly more complex sampling scheme also obeys the condition of *detailed balance*. Again we consider two states $m$ and $n$ with associated probabilities $\rho_m$ and $\rho_n$. Let us assume that the Rosenbluth weight of conformation $m$, $W_m$, is larger than $W_n$. In that case,

$$\begin{aligned} \alpha_{mn} &= P_n W_n / W_m \\ \alpha_{nm} &= P_m. \end{aligned} \tag{9}$$

It then follows immediately that the ratio of the transition rates from $m$ to $n$ and backwards, is

$$\frac{K_{mn}}{K_{nm}} = \frac{\rho_m P_n W_n / W_m}{\rho_n P_m}. \tag{10}$$

Again we see immediately that the condition of *detailed balance* is fulfilled.

A Monte Carlo scheme is ergodic if any two permissible configurations are connected with a nonzero probability using a finite number of moves from the set of allowed trial moves. We make no attempt to prove rigorously the ergodicity of the algorithm proposed here. However, we consider it plausible that the scheme is ergodic, for the following reasons. First, as the configurational bias scheme allows for direct conformational changes from any initial conformation to *any* trial conformation, it

satisfies, unlike many other schemes, the necessary ergodicity requirement for dynamic Monte Carlo schemes given by Madras and Sokal [14]. Second, the original self-avoiding walk of Rosenbluth and Rosenbluth [9] is ergodic, as are all other static random walk schemes. However, the Rosenbluth scheme corresponds to one possible type of move in the present sampling (namely a move where the trial conformation is regrown from the first unit). Clearly, any sampling scheme that includes an ergodic scheme as a subclass is itself ergodic.

## 3. Simulations

To test whether the Monte Carlo scheme proposed in the previous section is indeed efficient, we have carried out some tests on a very simple polymer system. Simulations were performed for a *single* selfavoiding polymer chain on a two-dimensional square lattice. For a single polymer in a periodic box we need to consider only moves that change the conformation of the polymer molecule, as uniform translations or rotations do not result in a distinct configuration. The only property of the polymer chain that we have considered is the mean-square end to end length. The calculations that we carried out had a twofold aim. First, we performed simulations for a wide range of chain lengths and densities with the aim of comparing these results with other simulations and finding the 'universal' exponent $\nu$ relating the mean-square end to end distance to the number $N$ of segments [17]

$$\langle R^2 \rangle \propto N^{2\nu}, \tag{11}$$

with $N$, the number of units in the chain. The second aim was to compare the performance of the present algorithm with that of existing simulation schemes. This comparison is discussed in section 3.2.

### 3.1. *N-dependence of* $\langle R^2 \rangle$

For this part of the work we have carried out a series of simulations with the number $N$ of units of our single polymer ranging from 8 to 441 at three different densities. The density or coverage of the system is controlled by the length of the periodic simulation cell ($N$ divided by the number of lattice sites in the cell). We studied the behaviour of the polymer chains at the following three densities; full coverage, approximately half coverage, and a free chain molecule, i.e., with the box length set to $N$.

The results of these simulations are summarized in the typical log $\langle R^2 \rangle$ versus log $N$ plots (figures 1–3). At all densities the graphs show the expected linear behaviour. Weighted linear least square fits [18] yield the following universal exponents $\nu$: $1{\cdot}560 \pm 0{\cdot}007$ for the free chain, $1{\cdot}360 \pm 0{\cdot}009$ for half coverage, and $1{\cdot}26 \pm 0{\cdot}03$ for full coverage (where we have taken the average of the 'odd' and 'even' $N$ points, see below). The deviation from the straight line for the longer chain molecules at the low and intermediate densities could be caused by the fact that, for small $N$, corrections to scaling effects become important and terms should be added to equation (11) as suggested by Meirovitch and Livne [19]. The values for $\langle R^2 \rangle$ for small $N$ have small standard errors and are therefore given higher weights in the linear fits. The reported values for $\nu$ could therefore be overestimates. Comparison of the value of $\nu$ of the free chain with previous simulation results for the same problem [9, 20] and with the theoretical prediction of 1·5 [17] show good agreement. For the half coverage simulations only $\langle R^2 \rangle$ for the chain molecule of 421 units deviates significantly from the

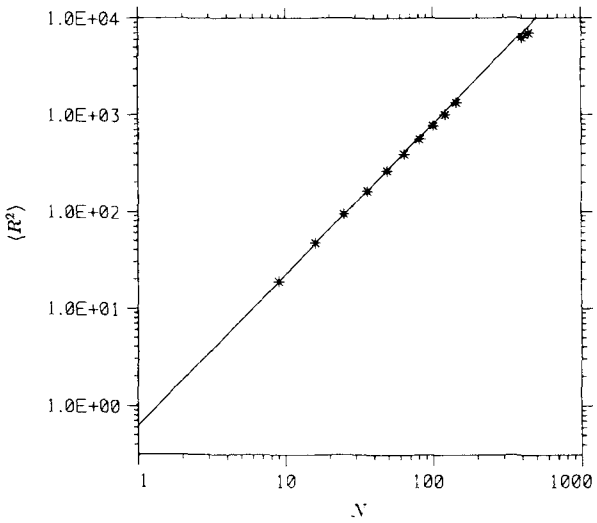


Figure 1. Log–log plot of the mean-square end to end length $\langle R^2 \rangle$ versus the number $N$ of units of a single polymer molecule on a square lattice for a free chain ($D = 0$).

straight line for the other chain lengths; this result has been omitted in the calculation of $\nu$. We were not able to find any results for this particular system in the literature, but one would expect the 'universal' exponent to decrease with increasing density, which is the case in our calculation. For the simulations at a density of unity the results are less clear cut. The $\langle R^2 \rangle$ values in figure 3 branch and show an even–odd effect depending on the length of the simulation box. We believe this feature to be an artefact caused by the simulation of a single chain molecule that will vanish for multichain systems. The value of $\nu$ for the even branch is $1{\cdot}30 \pm 0{\cdot}08$, and for the odd one $1{\cdot}21 \pm 0{\cdot}02$. It should be stressed that the quoted uncertainty in $\nu$ refers only to *statistical* errors. We have made no attempt to estimate the *systematic* errors caused by finite size effects.

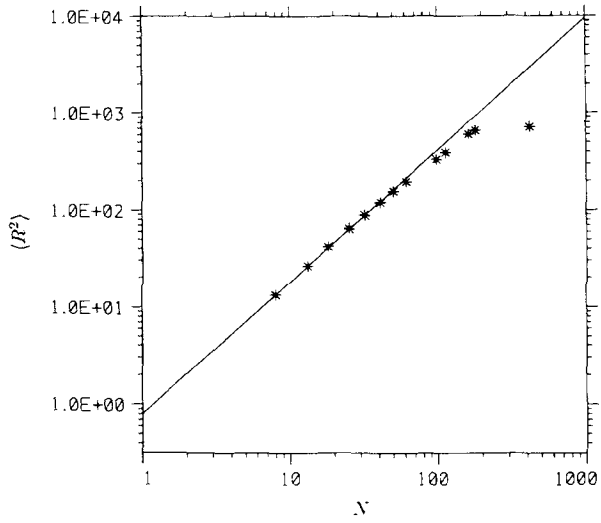


Figure 2. As figure 1, but for half coverage ($D \approx 0{\cdot}5$).

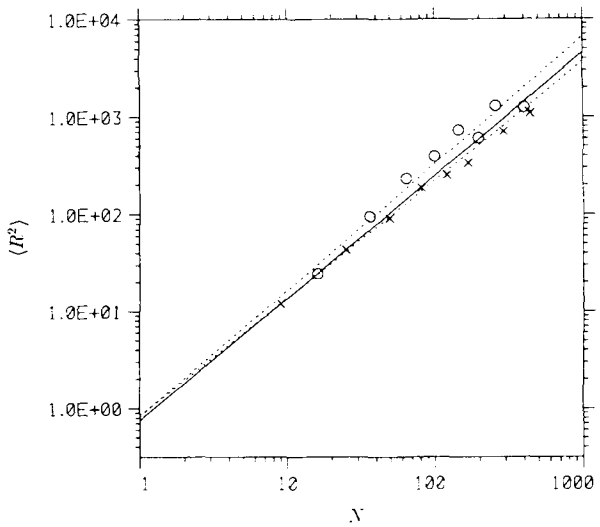


Figure 3. As figure 1, but for full coverage ($D = 1$); crosses for the values with odd number of units (odd box length), and circles for the values with even number of units (even box length).

### 3.2. *Performance of the configurational-bias Monte Carlo scheme*

This section focuses on the performance of different Monte Carlo schemes to achieve configurational equilibrium. As seen already from the results of section 3.1, the configurational bias scheme with the improved acceptance criterion works even at a density of unity. All other advanced simulation schemes except that of Pakula *et al.* [6] fail at this density. For comparison, we have also performed four short simulations of the same system as above, but using more conventional sampling schemes as follows. (a) A completely random walk algorithm (RW) with an excluded volume condition. In this very naïve sampling scheme the chain is generated step by step and every new unit is chosen randomly from the neighbouring lattice sites of the previous unit. Afterwards, the position of the new unit is checked for intra-chain overlap and the walk is terminated if an overlap occurs. (b) A non reversal random walk (NRRW) with an excluded volume condition. This scheme is similar to the RW, with the exception that backfolding for the next unit is not allowed. (c) The original self-avoiding random walk algorithm of Rosenbluth and Rosenbluth [8] (SAW). (d) A 'reptation' algorithm (REP), where a trial move consists of an attempt to move one-segment from the 'head' of the chain molecule to the 'tail', or vice versa [7].

Results for the four simulation techniques (a–d) have been compared with results of simulations obtained using both the acceptance criteria mentioned above, with the following abbreviations: RCB, for the scheme using the simple rejection criterion of equation (4) as the acceptance criterion, and MCB, for simulations following the improved 'Metropolis-like' acceptance criterion, equation (8). All programs have been kept as simple and general as possible: in particular, no neighbour table of any form or logical array that contains information about the occupancy of lattice sites has been used. To check the performance simulation, runs of the same length (approximately 1000 s of IBM 3084 CPU time) have been performed using all methods mentioned above. The standard error for a run has been estimated by dividing the run into ten blocks. The results are summarized in table 1, from which

Table. 1. Comparison of the results of $\langle R^2 \rangle$ and the corresponding standard errors of the mean, $\sigma_m$, for the six different simulation schemes. Values for the medium density simulations are 16/25 for $N = 9$, 49/64 for $N = 49$, and 144/169 for $N = 144$. The reptation scheme cannot be used at a density of unity; this is denoted by 'X' in the corresponding rows. Simulations that did not yield any successful generation of a chain or any successful conformational change have been marked with a dash.

| Program | $N$ | Free chain | Medium density | Full coverage |
|---|---|---|---|---|
| RW | 9 | 50·18 ± 0·33 | 32·05 ± 0·63 | 29·3 ± 1·2 |
| NRRW | | 47·269 ± 0·054 | 32·022 ± 0·025 | 22·57 ± 0·15 |
| SAW | | 47·261 ± 0·037 | 32·011 ± 0·033 | 22·493 ± 0·060 |
| REP | | 47·094 ± 0·084 | 32·037 ± 0·080 | X |
| RCB | | 47·280 ± 0·067 | 31·98 ± 0·21 | 27·4 ± 1·6 |
| MCB | | 47·252 ± 0·072 | 31·86 ± 0·17 | 25·49 ± 0·51 |
| RW | 49 | — | — | — |
| NRRW | | 263·8 ± 1·5 | — | — |
| SAW | | 263·7 ± 2·2 | 96·8 ± 3·6 | 76·6 ± 9·3 |
| REP | | 264·2 ± 2·2 | 106·9 ± 11·7 | X |
| RCB | | 261·2 ± 2·9 | 146 ± 21 | — |
| MCB | | 261·0 ± 1·2 | 115·5 ± 3·4 | 96·0 ± 6·3 |
| RW | 144 | — | — | — |
| NRRW | | — | — | — |
| SAW | | 1204 ± 142 | — | — |
| REP | | 1238 ± 36 | 335·5 ± 3·6 | X |
| RCB | | 828 ± 97 | 246 ± 19 | — |
| MCB | | 1377 ± 66 | 186 ± 31 | 565 ± 70 |

it can be seen that for the full coverage runs and for the runs with $N = 144$ the simulation were too short to yield good statistics. For some of the values we have results from the longer simulations described in section 3.1. These are 91·2 ± 1·5 for $N = 49, D = 1$; 1347 ± 21 for $N = 144, D = 0$; and 732 ± 37 for the same length at $D = 1$. It can be seen that, as chain length and density increase, the configurational bias scheme becomes more efficient than other schemes. From table 1 it is very difficult to decide if the new scheme is more efficient than the reptation algorithm; in particular, for $N = 144$ at the intermediate density, the reptation algorithm appears to yield an extremely small error. However, this small value of the error estimate may arise from the fact that most configurations calculated using the reptation algorithm are strongly correlated over long times and that therefore the block-averages obtained from the simulation are not independent.

As a check, long simulations using REP and MCB were performed for the medium densities. The lengths of these simulations were approximately 20 000 s for $N = 49$, and approximately 50 000 s for $N = 144$. As a test of the convergence of the two algorithms we have plotted the running average of $\langle R^2 \rangle$ versus the CPU time. This is shown in figures 4 and 5. From the plots it is clear that for the reptation scheme the configurations are indeed strongly correlated over times corresponding to the length of the earlier simulations (1000 s). For the longer chain there is no real convergence to a limiting value even after the full length of the simulation. This behaviour can be seen very well if we follow a 'movie' of the simulation; the configurations generated with the reptation algorithm sometimes get 'locked', i.e., oscillate between very similar configurations, for times of up to 15 000 s ($2 \times 10^7$ trial attempts). In contrast, the new scheme achieves reasonable results for $N = 144$ after some

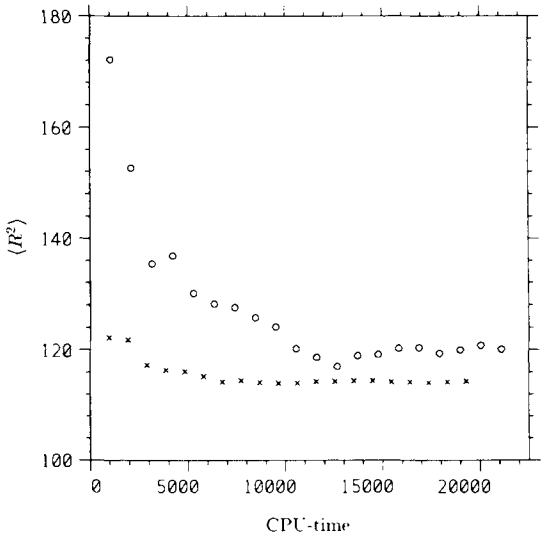


Figure 4. Plot of the mean-square end to end length $\langle R^2 \rangle$ as a function of the CPU-time. This plot is used to show the convergence for the results of the two most advantageous schemes for $N = 49$; crosses for the configurational bias scheme using the improved acceptance criterion, MCB, see equation (8), and circles for the reptation algorithm, REP.

10 000 s (300 000 trial moves). We have attempted to make a more quantitative comparison of the statistical error of both schemes. To this end we first computed the autocorrelation function of the statistical fluctuations [2]. From this function we can estimate the 'correlation time'. As expected, the MCB method does not yield significant correlations over the time-scale of this study; the effective correlation time is approximately 600 s. However, the reptation method yields strongly correlated results. Our estimate from the initial slope of the correlation function gives a correlation time between 10 000 and 15 000 s. The large uncertainty is due to the fact that

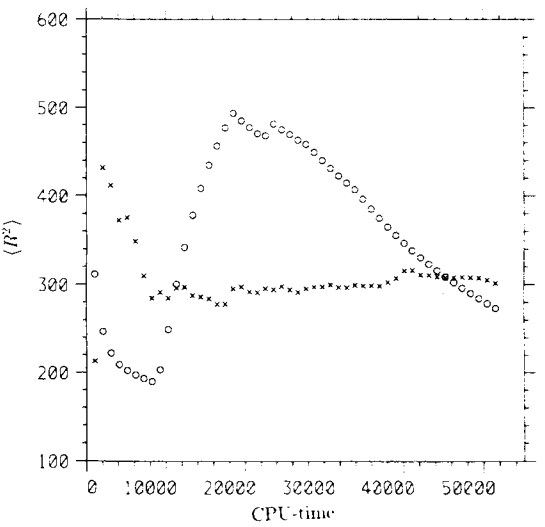


Figure 5. As figure 4, but for $N = 144$.

the correlation function shows large fluctuations for longer times. If we assume that for both methods the correlations decay exponentially we arrive at the following values of $\langle R^2 \rangle$ and the corresponding error estimates for a chain of 144 units and a simulation time of 50 000 s: 301 $\pm$ 21 for MCB and 270 $\pm$ 105 for REP. This implies that for the given example the reptation method would require roughly 25 times more CPU time than the new scheme to yield a result with similar accuracy. We expect the relative performance of the configurational-bias scheme to become even better at higher densities. On the other hand, due to ergodicity problems of the reptation scheme, it is not certain if the results of the reptation scheme are reliable at all. Even for free chains the nonergodicity of the reptation scheme has a minor influence on the computed values for $\langle R^2 \rangle$ as shown by Madras and Sokal [14]. If the density increases, the ergodicity problem becomes far more severe, and it is expected to have a stronger influence on the results.

## 4. Discussion and extensions

The configurational bias Monte Carlo scheme introduced in this paper does indeed appear to be more efficient than all other Monte Carlo schemes for chain molecules considered in this paper. In particular, at very high densities, it seems to be the only universal scheme that will work. In comparison, the cooperative motion algorithm of Pakula *et al.* [6] seems to be rather complicated, and it is most probably non-ergodic because it is based on a finite repertoire of local moves. Moreover, the cooperative motion algorithm cannot be used for nonlattice systems. In contrast, selfavoiding random walks are not limited to lattice systems, and the configurational-bias method can be easily extended to other situations [10]. This point is of particular importance because it is far from trivial to find a Monte Carlo scheme that works for long flexible molecules in continuous space [2].

Furthermore, the use of neighbour tables should increase the performance of our scheme much more than it would increase the speed of the other algorithms. This is due to the fact that, for example for the square lattice, our scheme MCB has to check for each step of the walk six lattice sites for their availability (three for the conformation that is generated and another three for the old conformation). In contrast, our simpler scheme, RCB, and the SAW scheme have to check three lattice sites; and all other schemes only one.

All the simulations described in this work deal with a single chain system only. Extending the scheme to multichain systems is straightforward, at least for all densities except the highest. If there are still some nonoccupied lattice sites available, the only modification required is that at the start of each trial attempt we have to select a chain molecule at random. In this case we do not need any other type of move because our scheme will change the conformations of all chain molecules and will in the process lead to translations and rotations of the polymers. At a reduced density of unity, where no empty sites are available in the simulation box, we will need a multichain configurational bias move. Configurational bias moves of a single molecule will only rearrange the conformation of the molecule under consideration within exactly the same space the chain occupied before. Clearly this alone would not lead to configurational equilibrium and would only sample a subset of the total phase space. We can, however, design a move that will allow us to sample the complete phase space. Instead of attempting to change only the conformation of one chain molecule we can regrow two or three neighbouring chains or parts thereof at the same

time. This has to be done in a step by step process, i.e., one unit is added in turn to each of the chains selected for the move until all chains have their former length.

Finally, we believe that the present scheme will allow us to study models for polymer systems that could not be examined before. An interesting application is to use the scheme for simulations of mixtures of chain molecules of different length. Thus far, all polymer simulations of mixtures have been confined to chains of the same length but different interaction potentials [3]. This is due to the very slow diffusion of the chains and the fact that all other schemes are unable to interchange chain molecules of different length. An extended configurational bias scheme could be used to swap parts of chain molecules in the simulation, thus allowing the change of a shorter molecule into a longer one and vice versa. Similarly, in combination with the chain insertion method previously proposed [10], we can perform simulations in the grand canonical and Gibbs ensemble which have been previously impossible for all but the shortest chain molecules.

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*Note added in proof*: We have recently become aware of a paper by J. Harris and S. A. Rice (1988, *J. chem. Phys.*, **88**, 1298) in which a simple version of the configurational-bias MC method on a lattice is used. We thank Dr H. Stettin for bringing this paper to our attention.

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